Bulk and surface switching in Mn-Fe-based Prussian blue analogues

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Supporting Information.

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1. Elemental Analysis

1.1. Experimental Details.

Experimental details on elemental analysis of samples A ($Rb_{0.97}Mn[Fe(CN)_6]_{0.98}\cdot 1.03H_2O$) and B ($Rb_{0.81}Mn[Fe(CN)_6]_{0.95}\cdot 1.24H_2O$) have been described previously.[1] For sample C ($Rb_{0.70}Cu_{0.22}Mn_{0.78}[Fe(CN)_6]_{0.86}\cdot 2.05H_2O$), elemental analysis of Rb, Mn, Cu, Fe (inductive coupling plasma atomic emission spectroscopy after demineralization in H_2SO_4/HNO_3), C, H (combustion above 850 °C and then IR detection) and N (combustion above 850 °C, then quantogravimetry) was performed at the analysis facility of CNRS in Vernaison, France.

1.2. Results.

Analytical data on all three samples are summarized in table I. Similar to the samples that were produced previously in analogous fashion[1], all three samples discussed here deviate from a perfect Rb:Mn(+Cu):Fe stoichiometry of 1:1:1. This deviation from the idealized

composition is ascribed to $[Fe(CN)_6]$-vacancies[1, 2, 3] which are filled by H_2O-molecules. This is consistent with the hydration found in the materials. As stated in the main text, the samples discussed here are consistent with the correlations in stoichiometry as found by Ohkoshi *et al.*[2] and Cobo *et al.*[3]

TABLE I: Observed and calculated weight percentages in samples A, B and C.

Sample	% Rb	% Mn	% Cu	% Fe	% C	% N	% H	proposed composition
A (obs.)[1]	22.75	15.09	0.00[2]	15.04	20.19	22.89	0.18	$Rb_{0.97}Mn[Fe(CN)_6]_{0.98}\cdot 1.03H_2O$
A (calc.)	22.75	15.08	0.00[2]	15.04	19.41	22.63	0.57	
B (obs.)[1]	19.97	15.83	0.00[2]	14.96	19.64	22.40	0.67	$Rb_{0.81}Mn[Fe(CN)_6]_{0.95}\cdot 1.24H_2O$
B (calc.)	19.97	15.83	0.00[2]	15.22	19.64	22.90	0.72	
C (obs.)[1]	17.73	12.71	4.23	14.32	18.79	20.62	1.51	$Rb_{0.70}Cu_{0.22}Mn_{0.78}[Fe(CN)_6]_{0.86}\cdot 2.05H_2O$
C (calc.)	17.73	12.71	4.23	14.32	18.48	21.55	1.23	

2. X-ray Powder Diffraction

2.1. Experimental Details.

Experimental details on X-ray powder diffraction of samples A ($Rb_{0.97}Mn[Fe(CN)_6]_{0.98}\cdot 1.03H_2O$) and B ($Rb_{0.81}Mn[Fe(CN)_6]_{0.95}\cdot 1.24H_2O$) have been described previously.[1] The X-ray powder diffraction pattern of sample C was recorded at room temperature and in Bragg-Brentano geometry, using a Bruker D8 Advance diffractometer operating with Cu K-α radiation using carefully grinded powder which was attached to the sample holder using vaseline. The 2θ range was from 10° to 70°, with a stepsize of 0.02° and an integration time of 4 seconds per step. The receiving slit had a width of 0.2°. The spectrum was then refined with a Rietveld structure refinement program [GSAS[4]].

2.2. Results.

X-ray diffraction patterns of samples A ($Rb_{0.97}Mn[Fe(CN)_6]_{0.98}\cdot 1.03H_2O$) and B ($Rb_{0.81}Mn[Fe(CN)_6]_{0.95}\cdot 1.24H_2O$) are available elsewhere.[1] The measured, fitted and difference powder diffraction profiles of sample C ($Rb_{0.70}Cu_{0.22}Mn_{0.78}[Fe(CN)_6]_{0.86}\cdot 2.05H_2O$) are shown in figure 1.

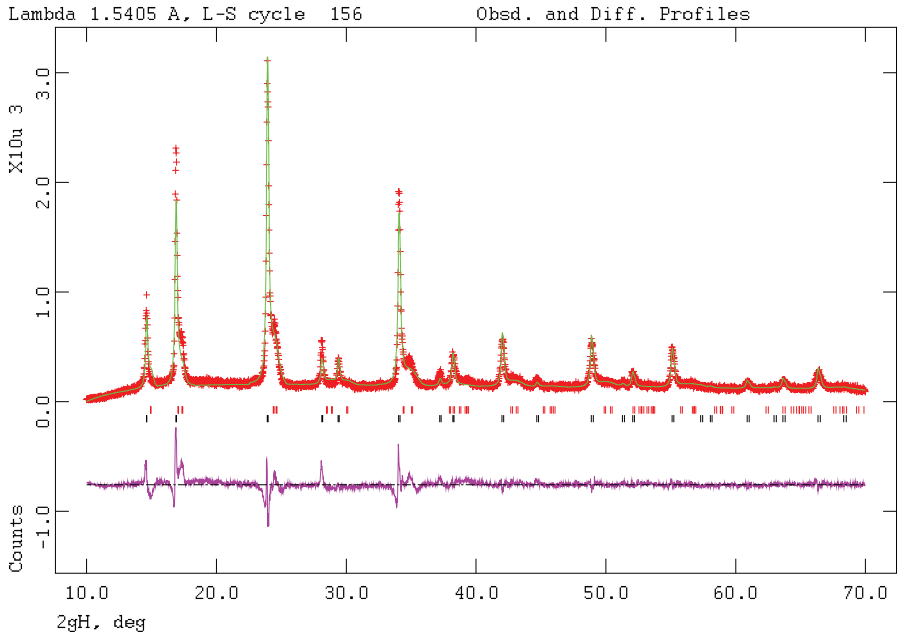

FIG. 1. Measured (red), fitted (green) and difference (purple) diffraction profiles of sample C ($Rb_{0.70}Cu_{0.22}Mn_{0.78}[Fe(CN)_6]_{0.86}\cdot 2.05H_2O$). Black marks indicate positions from the HT phase ($F\bar{4}3m$, see table II), red marks from the LT phase ($I\bar{4}m2$, see also table II)

The measured profile was fitted with two phases ('HT phase' and 'LT phase') which are found in table II. Selected details of the fit are found in table III. First, the measured profile was completely fitted with the $F\bar{4}3m$ phase as found by Moritomo *et al.*[5] The atom fractions were taken from the elemental analysis (see above), with the exception of the Rb and O atoms. For Rb, two positions are available in the $F\bar{4}3m$ phase: 4*c* and 4*d* (hereafter denoted position Rb1 and Rb2, respectively). Three scenarios were tried: all

Rb on position Rb1, all Rb on position Rb2 and both Rb positions equally populated. Of these scenarios the first scenario gave the best fit. Unfortunately, refining the Rb fractions led to an instable refinement. The O atoms were positioned on the Rb1 and Rb2 positions and on the N position. The fraction of the latter was kept constant at 0.14 (i.e. (1 - fraction N)), because we assume that all Cu and Mn atoms are surrounded by 6 ligands, which are either the CN-ligands or H_2O molecules. The fractions of the first two positions were allowed to vary. In this way, the refined O fraction per (Cu + Mn) was 1.95, which is close to the value of 2.05 as found by the elemental analysis. The Uiso values were allowed to vary accordingly: $\mathrm{Uiso_{Cu}} = \mathrm{Uiso_{Mn}} = \mathrm{Uiso_{Fe}}$, $\mathrm{Uiso_{C}} = \mathrm{Uiso_{N}} = \mathrm{Uiso_{O}}$. Refinement of the positions led to instable refinements. After refinement of the profile with the HT phase, some unassigned peaks were still present, most notably at 2θ values of 17.5°, 24.5° and 35°. These values are typical for the LT phase ($I\bar{4}m2$), as found by Moritomo *et al.*[6] When incorporating this second phase, all fractions of the atoms of both phases were kept constant and identical. The Uiso values of the LT phase were allowed to vary, but were kept identical for all atoms. The final weight fractions of HT phase and LT phase found were 80.4(8) % and 19.6(8) %, respectively. We realize that the fitted profile is not the best fit possible for the measured profile, but since several parameters could not be varied due to instability of the refinement, we are quite confident that the two phases (i.e. $F\bar{4}3m$ and $I\bar{4}m2$) represent the structure of sample C.

The obtained weight percentages of the HT and LT phases are quite close to the Mn and Cu fractions, respectively. The question arises whether the material is indeed a single phase solid solution $Rb_{0.70}Cu_{0.22}Mn_{0.78}[Fe(CN)_6]_{0.86}\cdot 2.05H_2O$, rather than a phase separated $Rb_xMn[Fe(CN)_6]_{\frac{(2+x)}{3}}\cdot zH_2O/Rb_xCu[Fe(CN)_6]_{\frac{(2+x)}{3}}\cdot zH_2O$ system. In order to exclude such phase separation, a $Rb_xCu[Fe(CN)_6]_{\frac{(2+x)}{3}}\cdot zH_2O$ sample was synthesized (synthesis practically identical to that of sample C, with 100% $CuCl_2$ instead of a 4:1 $MnCl_2$:$CuCl_2$ ratio). Elemental analysis (experimental details identical to those of sample C) revealed a $Rb_{0.35}Cu[Fe(CN)_6]_{0.80}\cdot 3.17H_2O$ stoichiometry (measured weight percentages: Rb 9.30%, Cu 19.91%, Fe 13.73%, C 18.02%, N 19.97%, H 2.15%). The measured, fitted and difference powder diffraction profiles this sample (procedure identical to that used for sample

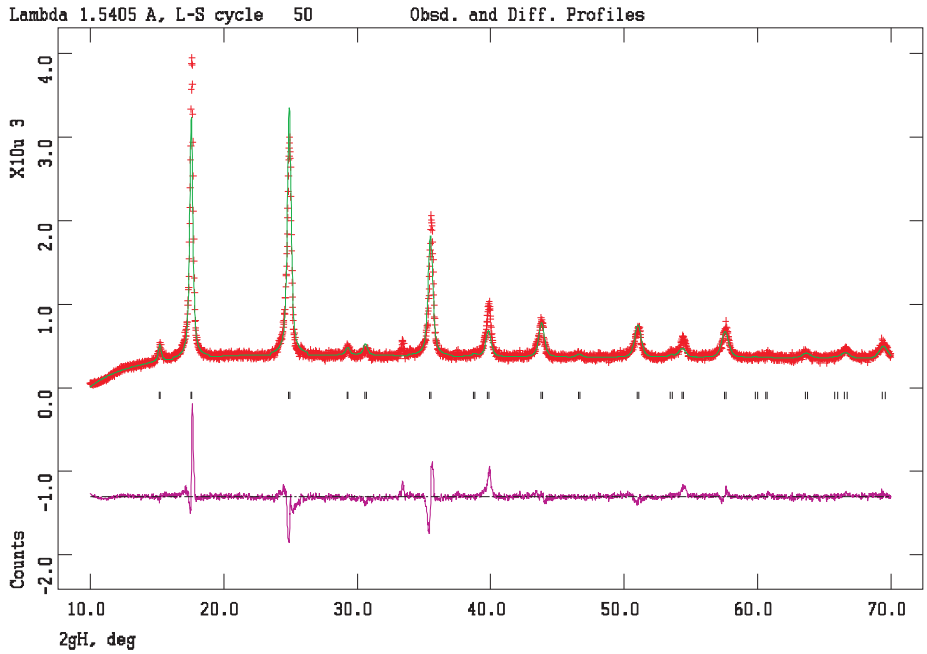

FIG. 2. Measured (red), fitted (green) and difference (purple) diffraction profiles of $Rb_{0.35}Cu[Fe(CN)_6]_{0.80}{\cdot}3.17H_2O$. Black marks indicate positions from the HT phase ($F\bar{4}3m$, see table IV)

C) are shown in figure 2. The measured diffraction profile was completely fitted with the $F\bar{4}3m$ phase. As for sample C, the atom fractions were taken from the elemental analysis, with the exception of the Rb and O atoms. These were placed in the interstitial sites and their fractions were allowed to fit in such a way that Rb1 + Rb2 = 0.35, Rb1 + O1 = 1 and Rb2 + O2 = 1. The Uisos of atoms on similar positions were kept equal. (I.e. $\mathrm{Uiso_{Fe}} = \mathrm{Uiso_{Cu}}$, $\mathrm{Uiso_{Rb1}} = \mathrm{Uiso_{Rb2}} = \mathrm{Uiso_{O1}} = \mathrm{Uiso_{02}}$ and $\mathrm{Uiso_{C}} = \mathrm{Uiso_{N}} = \mathrm{Uiso_{O3}}$). The positions of C, N and O3 were allowed to vary. The final fitted structure can be found in table IV and details of the fit can be found in table III. In a structure of symmetry $I\bar{4}m2$, one would expect additional diffraction peaks indexed as $h + k = (2n + 1)$, $h + l = (2n + 1)$, and $k + l = (2n + 1)$. Such additional peaks have been observed in the LT phase of many $Rb_xMn[Fe(CN)_6]_{\frac{(2+x)}{3}}{\cdot}zH_2O$ systems at 19° and 26°, for example. In this $Rb_{0.35}Cu[Fe(CN)_6]_{0.80}{\cdot}3.17H_2O$ system, however, we do not observe any of these extra peaks and we are able to index the whole diffraction pattern in $F\bar{4}3m$ symmetry, with

the exception of only one small peak (at 33.5°). It is presently unclear where this latter peak comes from. The above clearly shows that $Rb_xCu[Fe(CN)_6]_{\frac{(2+x)}{3}} \cdot zH_2O$ crystallizes in the $F\bar{4}3m$ space group rather than $I\bar{4}m2$, as is confirmed in numerous references in literature[7, 8, 9, 10], although other, related systems have been found to adopt a tetragonal structure[11]. Therefore, the possibility of phase separation being responsible for the fitted weight percentages in the diffraction profile of sample C is ruled out. Also, it shows sample C is in fact a solid solution and not a phase separated system.

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TABLE II: Atom parameters for the different phases of sample C at 295 K.

HT phase ($F\bar{4}3m$), weight fraction 80.4(8) %					
	Fraction	x	y	z	100 · Uiso
Cu	0.220	0.5	0.5	0.5	4.126±0.188
Mn	0.780	0.5	0.5	0.5	4.126±0.188
Fe	0.860	0	0	0	4.126±0.188
Rb	0.700	0.25	0.25	0.25	16.139±0.436
C	0.860	0.1822	0	0	7.268±0.355
N	0.860	0.2918	0	0	7.268±0.355
O1	0.225	0.25	0.25	0.25	7.268±0.355
O2	0.882	0.75	0.75	0.75	7.268±0.355
O3	0.140	0.2918	0	0	7.268±0.355
LT phase ($I\bar{4}m2$), weight fraction 19.6(8) %					
	Fraction	x	y	z	100 · Uiso
Cu	0.220	0	0	0.5	1.621±0.577
Mn	0.780	0	0	0.5	1.621±0.577
Fe	0.860	0	0	0	1.621±0.577
Rb1	0.700	0	0.5	0.25	1.621±0.577
C1	0.860	0	0	0.180	1.621±0.577
C2	0.860	0.2	0.2	0	1.621±0.577
N1	0.860	0	0	0.285	1.621±0.577
N2	0.860	0.311	0.311	0	1.621±0.577
O1	0.225	0	0.5	0.25	1.621±0.577
O2	0.882	0	0.5	0.75	1.621±0.577
O3	0.140	0	0	0.285	1.621±0.577
O4	0.140	0.311	0.311	0	1.621±0.577

TABLE III: Selected details of the fit of the powder diffraction profiles of $Rb_{0.70}Cu_{0.22}Mn_{0.78}[Fe(CN)_6]_{0.86}\cdot 2.05H_2O$ (sample C) and $Rb_{0.35}Cu[Fe(CN)_6]_{0.80}\cdot 3.17H_2O$.

$Rb_{0.70}Cu_{0.22}Mn_{0.78}[Fe(CN)_6]_{0.86}\cdot 2.05H_2O$ (Sample C)	
wRp	14.77 %
Rp	11.29 %
Weight fraction HT phase	80.4(8) %
Weight fraction HT phase	19.6(8) %
a (HT phase)	10.5463(8) Å
a (LT phase)	7.254(9) Å
b (LT phase)	10.45(3) Å
$Rb_{0.35}Cu[Fe(CN)_6]_{0.80}\cdot 3.17H_2O$	
wRp	10.13 %
Rp	7.23 %
Reduced χ^2	4.547 for 19 variables
a	10.141(1) Å
Fe-C distance	1.78(4) Å
Cu-N distance	2.17(6) Å
Cu-O distance	1.91(23) Å
C-N distance	1.13(9) Å

TABLE IV: Atom parameters for $Rb_{0.35}Cu[Fe(CN)_6]_{0.80}\cdot 3.17H_2O$.

space group ($F\bar{4}3m$), weight fraction 100 %					
	x	y	z	Fraction	$100 \cdot$ Uiso
Fe	0	0	0	0.80	3.6(3)
Cu	0.5	0.5	0.5	1.00	3.6(3)
Rb1	0.25	0.25	0.25	0.052(17)	7.8(4)
Rb2	0.75	0.75	0.75	0.298(17)	7.8(4)
C	0.175(4)	0	0	0.80	5.2(6)
N	0.287(6)	0	0	0.80	5.2(6)
O1	0.25	0.25	0.25	0.948(17)	7.8(4)
O2	0.75	0.75	0.75	0.702(17)	7.8(4)
O3	0.31(2)	0	0	0.20	5.2(6)